Spin-Selective Correlation Experiment for Measurement of Long-Range

J Couplings and for Assignment of (R/S) Enantiomers from the Residual

Dipolar Couplings and DFT

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# SUPPORTING INFORMATION

#### **<u>1.</u>** <u>C-HETSERF spectrum of the Cyclosporine A:</u>

The 800 MHz 2D C-HETSERF spectrum of cyclosporine A. Eight scans are accumulated for each one of the 200  $t_1$  increments and the number of the data points in  $t_2$  was set to 4608. The spectral widths in both dimensions were 7700 Hz. Prior to Fourier transformation, zero filling to 4K in F<sub>1</sub> and 16K points in F<sub>2</sub> and sine squared window function in both dimensions were applied. The recycle delay was set to 3.5 s



### **<u>2.</u>** <u>C-HETSERF spectrum of the (*R/S*)-propylene carbonate :</u>

The 2D C-HETSERF spectrum of (R/S)-propylene carbonate in PBLG/CDCl<sub>3</sub> solvent was recorded at 300 K. The delay  $\Delta$  was 1.8 ms. The flip angle used was 26°. Eight scans were accumulated for each of the 512  $t_1$  increments and the number of the data points in  $t_2$  was set to 8332. The spectral widths in both the F<sub>2</sub> and F<sub>1</sub> dimensions are 2000 Hz. Zero filling to 2048 in F<sub>1</sub> and 8192 points in F<sub>2</sub> and sine squared window function in both dimensions were applied before processing. The recycle delay was set to 3s. The eleven couplings used within the PALES program are given by the separations "a-i".





The separations "a-i" represent the couplings  $a={}^{3}T_{C1H6}$ ,  $b={}^{3}T_{C1H7}$ ,  $c={}^{2}T_{C1H5}$ ,  $d={}^{1}T_{C3H6}$ ,  $e={}^{1}T_{C3H7}$ ,  $f={}^{1}T_{C2H5}$ ,  $g={}^{2}T_{C2H6}$ ,  $h={}^{2}T_{C2H7}$ ,  $i={}^{2}T_{C3H5}$ , respectively for both the enantiomers. The magnitudes of couplings are given in the text.

### **<u>3.</u> INADEQUATE** experiment of the (R/S)-propylene carbonate :

All the two-dimensional <sup>13</sup>C-<sup>13</sup>C INADEQUATE spectra were recorded on an 800 MHz spectrometer at 300K using a recycle delay time of 3 sec. The spectral widths of 24 K Hz in  $F_1$  and 12 K Hz in  $F_2$  were used. 128 scans are accumulated for each of the 96  $t_1$  increments and the number of the data points in  $t_2$  was set to 776. Prior to Fourier transformation, zero filling to 512 in  $F_1$  and 2K points in  $F_2$  and sine squared window function in both dimensions were applied. The recycle delay was set to 4 s.

Traces from the two-dimensional <sup>13</sup>C-<sup>13</sup>C INADEQUATE experiment of (*R/S*)-propylene carbonate in both PBLG/CDCl3 solvent and CDCl<sub>3</sub>. The following figures show <sup>1</sup> $T_{CC}$  and <sup>1</sup> $J_{CC}$ .



# 4. Alignment tensor elements

The alignment tensor for the *R*-propylene carbonate in PBLG/CDCl<sub>3</sub> liquid crystalline phase. Below are the values of the alignment tensor for the RDCs of set-I fitted to *R*-structure.

n (RDC)	8	11	
Da/ Hz	-3.45 x 10 <sup>-3</sup>	-3.08 x 10 <sup>-3</sup>	
DaNH / Hz	-37.3	-33.3	
R	0.39	0.37	
Axx	7.15 x 10 <sup>-4</sup>	6.70 x 10 <sup>-4</sup>	
Ауу	2.74 x 10 <sup>-3</sup>	2.41 x 10 <sup>-3</sup>	
Azz	-3.45 x 10 <sup>-3</sup>	-3.08 x 10 <sup>-3</sup>	
EV Axx	-0.03; -0.34; 0.93	-0.01; -0.35; 0.93	
EV Ayy	0.78; -0.58; -0.18	0.78; -0.58; -0.21	
EV Azz	0.61; 0.73; 0.29	0.62; 0.72; 0.27	
RMSD	2.409	3.781	
CORR 0.995		0.988	

Da: axial component of alignment tensor and DaNH : axial component of the alignment tensor

normalized to NH vectors

R: rhombicity

Axx, Ayy, Azz: main axes of the alignment tensor

EV Axx, EV Ayy, EV Azz : Eigenvectors for the corresponding main axes of the tensor

n(RDC): number of RDCs used for the calculation of the parameters with PALES.

<u>5.</u>	Table 1. The experimental and back-calculated RDCs obtained using the optimized structure of R
	within the PALES.

Coupling	Set-I		Set-II	
	Experimental	<sup>a</sup> Theoretical	Experimental	<sup>b</sup> Theoretical
C1H5	2.0	-7.6	2.9	-7.3
C1H7	3.7	-5.7	3.3	-7.2
C1H6	2.3	-5.4	2.7	-6.1
С2Н5	27.7	27.5	26.3	26.5
C2H7	1.9	1.0	0.00	-1.9
С2Н6	2.0	-7.3	1.9	-9.9
С3Н5	2.5	0.3	3.1	-2.7
С3Н6	23.5	24.8	30.0	31.4
С3Н7	14.5	15.5	9.4	10.8
C1C2	-9.8	-8.9	-9.2	-8.4
C2C3	-7.7	-6.2	-10.7	-8.8

<sup>a</sup>theoretical RDCs when the eleven RDCs of Set-I are used

<sup>b</sup>theoretical RDCs when the eleven RDCs of Set-II are used.

Coupling	Set-I		Set-II	
	Experimental	<sup>a</sup> Theoretical	Experimental	<sup>b</sup> Theoretical
C2H5	27.7	27.0	26.3	25.5
C2H7	1.9	-8.6	0.00	0.5
C2H6	2.0	-7.7	1.9	-1.9
С3Н5	2.5	-0.6	3.1	2.6
С3Н6	23.5	25.3	30.0	30.8
С3Н7	14.5	15.4	9.4	10.2
C1C2	-9.9	-6.8	-9.2	-9.4
C2C3	-7.7	-9.8	-10.7	-9.6

**<u>6.</u>** Table 2. Tabulation of the each of experimental and back-calculated RDCs derived using the optimized structure of *S* enantiomer using the PALES.

<sup>a</sup>theoretical RDCs when the eight RDCs of Set-I were used. <sup>b</sup>theoretical RDCs when the eight RDCs of Set-II were used.

#### 7. Additional confirmation using SERF spectrum of (R/S)-propylene carbonate :



The SERF experiment for (R/S)-propylene carbonate was recorded and presented above. From the SERF spectrum, the outer triplet in the indirect dimension could be assigned to the Renantiomer whereas inner one for the S enantiomer as the sample is R enriched. Looking at intensities of different cross sections, peaks can be assigned unambiguously for R enantiomer in the direct dimension. The direct dimension represents the one dimensional proton spectrum of the methyl region. With the help of this information, the whole 2D spectrum could be assigned. The assignments obtained by this method are exactly same as what is described in this article. This further vindicates the applicability of the present method.